

IMPROVED SUPPORTS FOR HIGH SURFACE AREA CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of 35 U.S.C. 111(b) Provisional Application Serial No. 60/425,383 filed November 11, 2002, and US Provisional Application Serial No. 60/425,381 filed November 11, 2002, entitled "Novel Syngas Catalysts and Their Method of Use" which are hereby incorporated by reference herein for all purposes. This application is related to the concurrently filed, commonly owned, co-pending US Provisional Application Serial No. 60/501,185 filed September 8, 2003, entitled "Stabilized Alumina Supports, Catalysts Made Therefrom, And Their Use in Partial Oxidation."

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

TECHNICAL FIELD OF THE INVENTION

[0002] The present invention generally relates to catalyst supports having high surface area and stability in ultra high temperature conditions. This invention more particularly relates to modified alumina supports and catalysts made therefrom that maintain high surface areas at high temperature reaction conditions. The present invention also relates to processes employing these catalysts for the catalytic conversion of light hydrocarbons (e.g., natural gas) to produce carbon monoxide and hydrogen (synthesis gas), and conversion of synthesis gas to hydrocarbons. This invention also discloses methods of making such supports and catalysts.

BACKGROUND OF THE INVENTION

[0003] It is well known that the efficiency of catalyst systems is often related to the surface area on the support. This is especially true for systems using precious metal catalysts or other expensive catalysts. The greater the surface area, the more catalytic material is exposed to the reactants and the less time and catalytic material is needed to maintain a high rate of productivity.

[0004] Alumina (Al_2O_3) is a well known support for many catalyst systems. It is also well known that alumina has a number of crystalline phases such as alpha alumina (often

noted as α -alumina or α -Al₂O₃), gamma alumina (often noted as γ -alumina or γ -Al₂O₃) as well as a myriad of others. One of the properties of gamma alumina is that it has a very high surface area. This is commonly believed to be because the aluminum and oxygen molecules are in a crystalline structure or form that is not very densely packed. Unfortunately, when gamma alumina is heated to high temperatures, the structure of the atoms collapses such that the surface area decreases substantially. The most dense crystalline form of alumina is alpha alumina. Thus, alpha alumina has the lowest surface area, but is the most stable at high temperatures.

[0005] Alumina is ubiquitous as supports and/or catalysts for many heterogeneous catalytic processes. Some of these catalytic processes occur under conditions of high temperature, high pressure and/or high water vapor pressure.

[0006] It has long been a desire of those skilled in the catalyst support arts to create a form of alumina that has high surface area like gamma alumina and stability at high temperature like alpha alumina.

[0007] Such a catalyst support would have many uses. One such use is in the production of synthesis gas in a catalytic partial oxidation reactor. Synthesis gas is primarily a mixture of hydrogen and carbon monoxide and can be made from the partial burning of light hydrocarbons with oxygen. The hydrocarbons, such as methane or ethane are mixed with oxygen or oxygen containing gas and heated. When the mixture comes in contact with an active catalyst material at a temperature above an initiation temperature, the reactants quickly react generating synthesis gas and a lot of heat. Catalytic partial oxidation is a very fast reaction requiring only milliseconds of contact of reactant gases with the catalyst. As a result, it is quite exothermic causing reactor temperatures to exceed 800°C, often going above 1000°C and even sometimes going above 1200°C. Since catalysts used in the partial oxidation of hydrocarbons is typically supported, the support should be able to sustain this high thermal condition during long-term operation. In other words, a stable catalyst support which retains most of its surface area is desirable for long catalyst life.

[0008] The selectivity of catalytic partial oxidation of light hydrocarbons to the desired products, carbon monoxide and hydrogen, are influenced by several factors, but one of the most important of these factors is the catalyst composition. Noble metals typically serve as the best catalysts for the partial oxidation of methane. Noble metals are however

scarce and expensive, making their use economically challenging especially when the stability of the catalyst is questionable. One of the better known noble metal catalysts for catalytic partial oxidation is Rhodium. Rhodium-based syngas catalysts deactivate very fast due to sintering of both catalyst support and/or metal particles. Prevention of any of these undesirable phenomena is well-sought after in the art of catalytic partial oxidation process, particularly for successful and economical operation at commercial scale.

[0009] Another use for a highly stabilized, high surface area catalyst support would be in catalytic reactions that produce high temperature water vapor at high partial pressures. Such an environment challenges the hydrothermal stability of alumina supports making the supports more prone to degradation, fragmentation, or other processes that compromise the ability to support catalytic metals. For purposes of the present discussion, hydrothermal stability is defined as the property of resisting morphological and/or structural change in the face of elevated heat and water vapor pressure.

[0010] The Fischer-Tropsch process (also called the Fischer-Tropsch reaction or Fischer-Tropsch synthesis) is an example of a process that can generate water vapor of high partial pressure at high temperatures. The Fischer-Tropsch process comprises contacting a feed stream comprising syngas with a catalyst comprising typically a Group VIII metal at conditions of elevated pressure and temperature to produce mixtures of hydrocarbons and by-products comprising water and oxides of carbon. Syngas can be provided to a Fischer-Tropsch process from several sources such as the gasification of coal; from natural gas reserves using a partial oxidation process with an oxygen source; or by reaction of natural gas with steam (steam reforming).

[0011] It would therefore be highly desirable to create a thermally-stable high surface area support with a Group VIII metal loaded onto the support for highly productive long lifetime catalysts for the syngas production and/or its conversion to hydrocarbons.

SUMMARY OF THE INVENTION

[0012] The present invention is a thermally stable, high surface area alumina support with at least one modifying agent. The modifying agent is at least one element selected from the group consisting of aluminum, boron, silicon, gallium, selenium, rare earth metals, alkali earth metals and transition metals, and their corresponding oxides and ions. The inventive support has thermal stability at temperatures above 800°C.

[0013] The present invention also includes the process for stabilizing a high surface area alumina support. The process for stabilizing the support includes adding at least one modifying agent to the alumina prior to calcining. The modifying agents include aluminum, boron, silicon, gallium, selenium, rare earth metals, alkali earth metals and transition metals.

[0014] The invention further includes a catalyst comprising a catalytically active metal on an alumina support wherein the support includes at least one modifying agent. The modifying agent comprises at least one element selected from the group consisting of aluminum, boron, silicon, gallium, selenium, a rare earth metal, an alkali earth metal or a transition metal, their corresponding oxides or ions.

[0015] The present invention can be more specifically seen as a support, process and catalyst wherein the preferred modifying agents are lanthanide metals, aluminum, silicon, magnesium, calcium, manganese, cobalt, iron, zirconia, their oxides, their ions, or combinations thereof. The supported catalyst comprises at least one group VIII metal or rhenium with an optional promoter.

[0016] A more specific embodiment of the invention is a catalyst having a high surface area thermally stable alumina support with at least one group VIII metal or rhenium and an optional promoter loaded onto the support. Another specific embodiment of the invention is a catalyst having a high surface area hydro-thermally stable alumina support modified with aluminum with at least one group VIII metal and an optional promoter loaded onto the support.

[0017] More particularly, the invention relates to processes for the catalytic partial oxidation of light hydrocarbons (*e.g.*, methane or natural gas) to produce primarily synthesis gas and the use of such supported catalysts to make carbon monoxide and hydrogen under conditions of high gas hourly space velocity, elevated pressure and high temperature.

[0018] The present invention further relates to Fischer-Tropsch catalysts and processes for the conversion of syngas for producing C₅+ hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] For a more detailed understanding of the preferred embodiments, reference is made to the accompanying drawings, wherein:

Figure 1 represents the pore distribution of unmodified Al_2O_3 and several examples of modified Al_2O_3 ;

Figure 2 represents X-ray diffraction traces of the unmodified Al_2O_3 and several modified Al_2O_3 after calcinations at 1100°C ; and

Figure 3 represents the performance data for syngas production from a catalyst made according to a preferred embodiment of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0020] Herein will be described in detail, specific embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various embodiments of the present invention provide a number of different configurations of the overall gas to liquid conversion process.

[0021] The present invention provides a modified alumina support with enhanced thermal stability and with a high BET surface area greater than $5 \text{ m}^2/\text{g}$, preferably greater than $10 \text{ m}^2/\text{g}$, and preferably greater than $15 \text{ m}^2/\text{g}$. The modified alumina support is obtained by deposition of at least one modifying agent. The modifying agent comprises at least one element selected from the group consisting of aluminum, boron, silicon, gallium, selenium, rare earth metals, transition metals, alkali earth metals, and their corresponding oxides or ions, preferably selected from the group consisting of alumina (Al), boron (B), silicon (Si), gallium (Ga), selenium (Se), calcium (Ca), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), zirconium (Zr), iron, (Fe), cobalt (Co), manganese (Mn), magnesium (Mg), and their corresponding oxides or ions. More preferably the modifying agent comprises La, Al, Sm, Pr, Ce, Eu, Yb, Si, Ce, Mg, Ca, Mn, Co, Fe, Zr, their corresponding oxides or ions, or any combinations thereof. Most preferably the modifying agent comprises La, Al, Sm, Pr, Ce, Eu, Yb, Si, Mg, Co, their corresponding oxides or ions, or any combinations thereof.

[0022] The present invention provides a method of making a modified alumina support with a modifying agent. The method comprises the deposition of the modifying agent followed by a high temperature treatment. The high temperature treatment is a calcination at a temperature greater than 400°C. The calcination temperature is selected based on the highest temperature the catalyst would likely experience in operation, *i.e.* the catalytic reactor. Thus, if the catalytic system is anticipated to operate at a temperature above 800°C, the calcination temperature would be greater than 600°C, preferably between 800°C and 1400°C, more preferably between 900°C and 1300°C. If the catalytic system is anticipated to operate at less 800°C, the calcination range would preferably be between about 400°C and 800°C, more preferably between 450°C and 750°C.

[0023] In preferred embodiments the stabilized support is made by a method that comprises combining the modifying agent or a precursor thereof with an alumina material or a precursor of an alumina material in an amount sufficient to deter disintegration or structural deterioration of the alumina material during the partial oxidization process. In certain embodiments the combined modifying agent and alumina material form a solid solution between the modifying agent and at least a portion of the support material. As a result, a modifier-support intermediate structure is obtained. In certain preferred embodiments the stabilized support comprises, at least in part, a crystalline structure that is capable of resisting a phase change at temperatures up to at least 1,200°C. The modifying agent may comprise, for example, La, Al, Sm, Pr, Ce, Eu, Yb, Si, Mg, Co, Ca, Mn, Fe or Zr.

[0024] In certain embodiments the syngas catalyst is prepared by a method that comprises calcining the modifier-support intermediate at a temperature in the operating temperature range of the catalyst when the catalyst is used in a reactor for catalyzing the partial oxidation of the light hydrocarbon to form carbon monoxide and hydrogen. After the catalytic material is deposited on the stabilized support, it may be reduced by subjecting the catalyst to reducing conditions. In some embodiments, the catalytic material comprises rhodium, and in certain embodiments comprises a rhodium alloy such as Rh-Ru or Rh-Ir, for example.

[0025] In certain embodiments the modifying agent comprises 0.1 - 10 wt% of the catalyst, and in some embodiments it comprises 1 - 5 wt% of the catalyst. In some embodiments,

the modifying agent comprises cobalt, magnesium, or silicon, and in some embodiments the modifying agent comprises lanthanum.

[0026] Modifying alumina (Al_2O_3) with some rare earth metals has been proven to be effective in stabilizing the surface area of modified Al_2O_3 . It was discovered by the Applicants that doping a $\gamma\text{-Al}_2\text{O}_3$ with lanthanum oxide (La_2O_3) inhibits or retards the phase transformation of γ phase to θ phase and eventually to α phase and thus stabilizes the surface area and pore structure of the alumina material even at high calcination temperatures above 1000°C .

[0027] The support can have different forms such as monolith or particulate or have discrete or distinct structures. The term "monolith" as used herein is any singular piece of material of continuous manufacture such as solid pieces of metal or metal oxide or foam materials or honeycomb structures. The terms "distinct" or "discrete" structures or units, as used herein, refer to supports in the form of divided materials such as granules, beads, pills, pastilles, pellets, cylinders, trilobes, extrudates, spheres or other rounded shapes, or another manufactured configuration. Alternatively, the divided material may be in the form of irregularly shaped particles. Preferably at least a majority (*i.e.*, $>50\%$) of the particles or distinct structures have a maximum characteristic length (*i.e.*, longest dimension) of less than six millimeters, preferably less than three millimeters. An especially preferred particle size range is about 0.18 millimeters (80 mesh) to about 3 millimeters, more preferably about 0.3-1.4 millimeters (about 14-50 mesh). The term "mesh" refers to a standard sieve opening in a screen through which the material will pass, as described in the Tyler Standard Screen Scale (C.J. Geankoplis, TRANSPORT PROCESSES AND UNIT OPERATIONS, Allyn and Bacon, Inc., Boston, MA, p. 837), hereby incorporated herein by reference. Mesh size of the particles or distinct structures can be measured by the ASTM E-11-61 method.

[0028] The present invention also relates to improved catalyst compositions using a modified alumina support, as well as methods of making and using them. In particular, some embodiments of the present invention comprise high melting point catalysts comprising metal alloys.

[0029] The catalyst is supported on a modified alumina with a minimum BET surface area of $5\text{ m}^2/\text{g}$, preferably greater than $10\text{ m}^2/\text{g}$, more preferably greater than $15\text{ m}^2/\text{g}$ after high

heat treatment. Preferably the modified alumina is modified with aluminum, cobalt, magnesium, silicon, a lanthanide metal, their respective oxide or ion such as for example, aluminum, lanthanum, samarium, cobalt, magnesium, silicon, or their respective oxide or ion. Without wishing to be bound to a particular theory, the Applicants believe that the metal-support interaction in catalysts supported on for example La_2O_3 -modified Al_2O_3 is stronger than that in the catalyst supported on unmodified Al_2O_3 , and that this strong metal-support interaction in La_2O_3 -modified Al_2O_3 supported catalysts might be responsible for the unusually high catalyst stability.

[0030] The catalyst used for producing synthesis gas comprises an active metal selected from the group consisting of Group VIII metals, rhenium, tungsten, zirconium, molybdenum, and any mixtures thereof. Preferably the catalyst used for producing synthesis gas comprises rhodium (Rh), ruthenium (Ru), iridium (Ir), rhenium (Re) or any combination thereof. In some embodiments, the active metal is comprised in an alloy form, preferably a rhodium alloy. Although not wishing the scope of this application to be limited to this particular theory, the Applicants believed that alloying rhodium with other metals appears to sustain the resistance of rhodium catalysts to sintering, and therefore to allow the Rh alloy catalysts to deactivate at a slower rate than syngas catalysts containing only rhodium. Suitable metals for the rhodium alloy generally include but are not limited to Group VIII metals, as well as rhenium, tantalum, niobium, molybdenum, tungsten, zirconium and mixtures thereof. The preferred metals for alloying with rhodium are ruthenium, iridium, platinum, palladium, tantalum, niobium, molybdenum, rhenium, tungsten, cobalt, and zirconium, more preferably ruthenium, rhenium, and iridium.

[0031] The catalyst used for converting synthesis gas comprises an active metal selected from Group VIII. Preferably the catalyst used for converting synthesis gas comprises cobalt, iron, ruthenium, nickel or any combination thereof. In preferred embodiments, the modifying agent is aluminum or an oxide or ion of aluminum.

[0032] In accordance with the present invention, the loading of the active metal is preferably between 0.1 and 50 weight percent of the total catalyst weight (herein wt%).

[0033] In one embodiment of the invention the active metal is rhodium, which comprises from about 0.1 to about 20 wt % of the catalyst material, preferably from about 0.5 to about 10 wt %, and more preferably from about 0.5 to about 5 wt %. When a rhodium alloy is

used, the other metal in the rhodium alloy preferably comprises from about 0.1 to about 20 wt % of the catalyst material, preferably from about 0.5 to about 10 wt %, and more preferably from about 0.5 to about 5 wt %.

[0034] When the active metal is cobalt, nickel, or iron, the metal comprises from about 0.1 to 50 wt% of the catalyst material, preferably from about 5 to about 40 wt %, and more preferably from about 10 to about 35 wt %.

[0035] In another embodiment of the invention the active metal is ruthenium which comprises from about 0.1 to 15 wt % of the catalyst material, preferably from about 1 to about 8 wt %, and more preferably from about 2 to about 5 wt %.

[0036] The catalyst structure employed is characterized by having a high metal surface area, *i.e.*, at least 0.8 square meters of metal per gram of catalyst structure, preferably at least 1 m²/g. Preferably the metal is rhodium and the rhodium surface area at least 0.8 square meters of rhodium per gram of supported catalyst, preferably at least 1 m²/g.

[0037] Catalyst compositions may also contain one or more promoters. In some embodiments when one active metal is rhodium, rhenium, ruthenium, or iridium, the promoter comprises an element selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, preferably Sm, Eu, Pr and Yb. The Applicants discovered that the introduction of a lanthanide oxide, especially Sm₂O₃, on the modified alumina support surface before deposition of active metal(s) seems to further enhance the metal-support interaction, and that the active metal(s) also disperses better on the surface of Al₂O₃ modified with La₂O₃ and/or Sm₂O₃. According to some embodiments with the use of a rhodium alloy, the presence of a promoter metal can be omitted without detriment to the catalyst activity and/or selectivity. It is foreseeable however that, in some alternate embodiments, a promoter could be added to a catalyst material comprising a rhodium alloy. In other embodiments the active metal is cobalt, ruthenium, iron, or nickel, and the promoter is selected from the group consisting of the alkali metals, the alkaline earths, the lanthanides, Group IIIB, IVB, VB, VIB and VIIB metals. Promoters, when used, preferably comprise about 1-15 wt % of the catalyst composition.

[0038] In one embodiment of the present invention is more preferably directed towards syngas catalysts used in partial oxidation reactions and even more preferably used in syngas catalysts that contain solely rhodium or rhodium alloys. However, it should be

appreciated that the catalyst compositions according to the present invention are useful for other partial oxidation reactions, which are intended to be within the scope of the present invention.

[0039] In another embodiment of the present invention the catalyst support is used for hydrogenation catalysts in conversion of syngas to alcohols or C₅₊ hydrocarbons via the Fischer-Tropsch reaction. In addition, the present invention contemplates an improved method for converting hydrocarbon gas to liquid hydrocarbons using the novel syngas catalyst compositions described herein. Thus, the invention also relates to processes for converting hydrocarbon-containing gas to liquid products via an integrated syngas to Fischer-Tropsch, methanol or other process.

Method of preparation of catalyst support

[0040] The present invention further presents a method of making a syngas catalyst support wherein said method comprises depositing a compound or precursor of a modifying agent onto an alumina precursor; calcining the deposited alumina precursor at temperatures temperature greater than 600°C, preferably between 800°C and 1400°C, more preferably between 900°C and 1300°C to form a modified alumina.

[0041] The present invention further presents a method of making a Fischer-Tropsch catalyst support wherein said method comprises depositing a compound or precursor of a modifying agent onto an alumina precursor; calcining the deposited alumina precursor at temperatures temperature between 300°C and 1000°C, and more preferably at a temperature between 400°C and 800°C to form a modified alumina.

[0042] The alumina precursor can comprise one or more alumina phases such as, but not limited to, gamma, delta, kappa, theta, alpha that are known in the art. The alumina precursor can also comprise Boehmite alumina or pseudoboehmite. An alumina precursor comprising mainly γ -alumina is preferred. It should be understood that the alumina precursor could be pre-treated prior to deposition of the modifying agent. The pre-treatment could be heating, spraydrying (to *e.g.*, adjust particle sizes) dehydrating, drying, steaming or calcining. Steaming the alumina precursor can be done at conditions sufficient to transform the alumina precursor into a hydrated form of aluminum oxide, such as boehmite or pseudoboehmite.

[0043] The present process for preparing a modified alumina may further comprise steaming the deposited alumina precursor at conditions sufficient to transform the deposited alumina precursor into a modified boehmite alumina wherein steaming is defined as subjecting a given material, within the confines of an autoclave or other suitable device, to an atmosphere comprising a saturated or under-saturated water vapor at conditions of elevated temperature and elevated water partial pressure.

[0044] In one aspect, the steaming of the deposited alumina precursor is preferably performed at a temperature ranging from 150°C to 500°C, more preferably ranging from 180°C to 300°C, and most preferably ranging from 200°C to 250°C; a water vapor partial pressure preferably ranging from 1 bar to 40 bars, more preferably ranging from 4 bars to 20 bars, and most preferably from 10 bars to 20 bars; and an interval of time preferably from 0.5 hour to 10 hours, and most preferably 0.5 hour to 4 hours. Preferably, under these steaming conditions, the deposited alumina precursor is at least partially transformed to at least one phase selected from the group boehmite, pseudoboehmite and the combination thereof. A pseudoboehmite alumina refers to a monohydrate of alumina having a crystal structure corresponding to that of boehmite but having low crystallinity or ultrafine particle size. Alternatively, the optional steaming of the deposited alumina precursor may comprise same conditions of temperature and time as above, but with a reduced water vapor partial pressure preferably ranging from 1 bar to 5 bar, and more preferably ranging from 2 bars to 4 bars.

[0045] The compound or precursor of a modifying agent can be in the form of salt, acid, oxide, hydroxide, oxyhydroxide, carbide, and the like. Preferably the compound or precursor of a modifying agent is an oxide or a salt (such as carbonate, acetate, nitrate, chloride, or oxalate). The modifying agent comprises at least one element selected from the group consisting of aluminum, boron, silicon, gallium, selenium, rare earth metals, transition metals, alkali earth metals, their corresponding oxides or ions, preferably at least one element selected from the group consisting of Al, B, Si, Ga, Se, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and their corresponding oxides or ions. More preferably, the modifying agent comprises either La, Al, Pr, Ce, Eu, Yb, or Sm, or their corresponding oxides or ions, or any combinations thereof. Preferably the compound or precursor of a modifying agent is a nitrate salt or a chloride salt, as for example only

La(NO₃)₃, or Al(NO₃)₃. It should be understood that more than one modifying agent or more than one compound or precursor of a modifying agent can be used.

[0046] The modifying agent can be deposited into the alumina precursor by means of different techniques. For example only, deposition methods can be spraydrying, impregnation, co-precipitation, chemical vapor deposition, and the like. It should also be understood that any combination of techniques or multiple steps of the same technique can be used to deposit a modifying agent. One preferred technique for depositing the modifying agent is impregnation, particularly incipient wetness impregnation.

[0047] When the deposition is done via impregnation, optionally a drying step at temperatures between 75°C and 150°C is performed on the deposited alumina prior to calcination. In another embodiment, the modified support is derived from the alumina precursor by contacting the alumina precursor with the modifying agent so as to form a support material and treating the support material so as to form a hydrothermally stable support. Contacting the alumina precursor with the structural stabilizer preferably includes dispersing the alumina precursor in a solvent so as to form a sol, adding a compound of the modifying agent to the sol, and spraydrying the sol so as to form the support material. It should be understood that more than one modifying agents or more than one compound or precursors of a modifying agent can be added to the sol. Alternatively, one modifying agent can be incorporated into the support by means of the aforementioned techniques. Alternatively, two or more modifying agents can be incorporated into the support by means of the aforementioned techniques.

Method of catalyst preparation

[0048] The present invention further presents a method of making a syngas catalyst wherein said method comprises optionally depositing a compound or precursor of one or more promoters to the modified alumina and calcining the (deposited) modified alumina at temperatures greater than 600°C, preferably between about 800°C and about 1400°C, more preferably between about 900°C and about 1300°C to form a catalyst precursor; depositing a compound or precursor of one or more active metals to the catalyst precursor; calcining the deposited catalyst precursor at temperatures between about 300°C and about 1200°C, preferably between about 500°C and about 1100°C.

[0049] The compound or precursor of the promoter can be in the form of salt, acid, oxide, hydroxide, oxyhydroxide, carbide, and the like. Preferably the compound or precursor of a promoter is a salt. The promoter comprises at least one element selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and their corresponding oxides or ions. Preferably the promoter comprises either Pr, Yb, Eu, Sm, their corresponding oxides or ions, or any combinations thereof. Preferably the compound or precursor of a promoter is a nitrate salt, as for example only $\text{Sm}(\text{NO}_3)_3$ or $\text{La}(\text{NO}_3)_3$. It should be understood that more than one promoter or more than one compound or precursor of a promoter can be used.

[0050] The present invention further includes a method of making a FT catalyst wherein said method comprises optionally depositing a compound or precursor of one or more promoters to the modified alumina and calcining the (deposited) modified alumina at temperatures greater than 250°C , preferably between about 300°C and about 800°C to form a catalyst precursor; depositing a compound or precursor of one or more active metals to the catalyst precursor; calcining the deposited catalyst precursor at temperatures between about 250°C and about 800°C , preferably between about 300°C and about 800°C . The promoter comprises at least one element selected from the group consisting of alkali metals, the alkaline earths, the lanthanides, Group IIIB, IVB, VB, VIB and VIIB metals, their corresponding oxides or ions, or any mixtures thereof. Preferably, the promoter comprises either Pt, Pd, Re, Ru, Ag, B, Au, Cu, their corresponding oxides or ions, or any combinations thereof. The compound or precursor of the promoter can be in the form of salt, acid, oxide, hydroxide, oxyhydroxide, carbide, and the like. Preferably the compound or precursor of a promoter is a salt, for example only $\text{Co}(\text{NO}_3)_3$.

[0051] The promoter can be deposited into the modified alumina by means of different techniques. For example only, deposition methods can be impregnation, co-precipitation, chemical vapor deposition, and the like. The preferred technique for depositing the promoter is impregnation.

[0052] When the deposition of the promoter is done via impregnation, optionally a drying step at temperatures between 75°C and 150°C is performed on the deposited modified alumina prior to calcination.

[0053] The compound or precursor of the active metal can be in the form of salt, acid, oxide, hydroxide, oxyhydroxide, carbide, and the like. Preferably the compound or precursor of the active metal is a salt. The active metal comprises one element selected from the group consisting of Group VIII metals, rhenium, tungsten, zirconium, their corresponding oxides or ions, and any combinations thereof. Preferably the active metal for syngas catalyst comprises either rhodium, iridium, ruthenium, their corresponding oxides or ions, or any combinations thereof. Preferably the compound or precursor of the active metal is a nitrate or a chloride salt, as for example only $\text{Rh}(\text{NO}_3)_3$ or RhCl_3 . Preferably the active metal for FT catalyst comprises either cobalt, ruthenium, iron, nickel, their corresponding oxides or ions, or any combinations thereof. It should be understood that more than one active metal or more than one compound or precursor of an active metal can be used. When two active metals are used in the syngas catalyst, it is preferred that at least rhodium is selected as one metal, that the other metal is selected from the active metal list above for syngas catalyst, and that the loading of both metals is such so as to form a rhodium alloy.

[0054] The active metal can be deposited on the catalyst precursor (promoted or unpromoted modified alumina) by means of different techniques. For example only, deposition methods can be impregnation, co-precipitation, chemical vapor deposition, and the like. The preferred technique for depositing the active metal is impregnation.

[0055] When the deposition of the active metal is done via impregnation, optionally a drying step at temperatures between 75°C and 150°C is performed on the deposited catalyst precursor prior to calcination.

Process of Producing Syngas

[0056] According to the present invention, a syngas reactor can comprise any of the synthesis gas technology and/or methods known in the art. The hydrocarbon-containing feed is almost exclusively obtained as natural gas. However, the most important component is generally methane. Natural gas comprise at least 50% methane and as much as 10% or more ethane. Methane or other suitable hydrocarbon feedstocks (hydrocarbons with four carbons or less) are also readily available from a variety of other sources such as higher chain hydrocarbon liquids, coal, coke, hydrocarbon gases, etc., all of which are clearly known in the art. Preferably, the feed comprises at least about 50% by volume

methane, more preferably at least 80% by volume; and most preferably at least 90% by volume methane. The feed can also comprise as much as 10% ethane. Similarly, the oxygen-containing gas may come from a variety of sources and will be somewhat dependent upon the nature of the reaction being used. For example, a partial oxidation reaction requires diatomic oxygen as a feedstock, while steam reforming requires only steam. According to the preferred embodiment of the present invention, partial oxidation is assumed for at least part of the syngas production reaction.

[0057] Regardless of the source, the hydrocarbon-containing feed and the oxygen-containing feed are reacted under catalytic conditions. Improved catalyst compositions in accordance with the present invention are described herein. They generally are comprised of a catalytic metal, some alloyed, that has been reduced to its active form and with one or more optional promoters on a modified alumina support structure.

[0058] It has been discovered that the modification of alumina by a modifying agent selected from the lanthanide metals group particularly, results in a catalytic support suitable for high-temperature reactions such as syngas production via partial oxidation.

[0059] The syngas catalyst compositions according to the present invention comprise an active metal selected from the group consisting of Group VIII metals, rhenium, tungsten, zirconium, their corresponding oxides or ions, and any combinations thereof, preferably a group VII metal or rhenium, more preferably rhodium, iridium, ruthenium, rhenium, or combinations thereof.

[0060] In some embodiments when the active metal is rhodium, rhodium is comprised in a high melting point alloy with another metal. It has been discovered that in addition to the enhanced thermal stability of the support, the high melting point rhodium alloys used in some of these syngas catalysts confer additional thermal stability than non-alloy rhodium catalysts, which leads to enhanced ability of the catalyst to resist various deactivation phenomena.

[0061] It is well known that during syngas reactions, several undesired processes, such as coking (carbon deposition), metal migration, and sintering of metal and/or the support, can occur and severely deteriorate catalytic performance. The catalyst compositions of the present invention are better able to resist at least one of these phenomena over longer periods of time than prior art catalysts. As a consequence, these novel rhodium

containing catalysts on modified alumina can maintain high methane conversion as well as high CO and H₂ selectivity over extended periods of time with little to no deactivation of the syngas catalyst.

[0062] The support structure of these catalysts can be in the form of a monolith or can be in the form of divided or discrete structures or particulates. Particulates are preferred. Small support particles tend to be more useful in fluidized beds. Preferably at least a majority (*i.e.*, >50%) of the particles or distinct structures have a maximum characteristic length (*i.e.*, longest dimension) of less than six millimeters, preferably less than three millimeters. According to some embodiments, the divided catalyst structures have a diameter or longest characteristic dimension of about 0.25 mm to about 6.4 mm (about 1/100" to about 1/4"), preferably between about 0.5 mm and about 4.0 mm. In other embodiments they are in the range of about 50 microns to 6 mm.

[0063] The hydrocarbon feedstock and the oxygen-containing gas may be passed over the catalyst at any of a variety of space velocities. Space velocities for the process, stated as gas hourly space velocity (GHSV), are in the range of about 20,000 to about 100,000,000 hr⁻¹, more preferably of about 100,000 to about 800,000 hr⁻¹, most preferably of about 400,000 to about 700,000 hr⁻¹. Although for ease in comparison with prior art systems space velocities at standard conditions have been used to describe the present invention, it is well recognized in the art that residence time is the inverse of space velocity and that the disclosure of high space velocities corresponds to low residence times on the catalyst. "Space velocity," as that term is customarily used in chemical process descriptions, is typically expressed as volumetric gas hourly space velocity in units of hr⁻¹. Under these operating conditions a flow rate of reactant gases is maintained sufficient to ensure a residence or dwell time of each portion of reactant gas mixture in contact with the catalyst of no more than 200 milliseconds, preferably less than 50 milliseconds, and still more preferably less than 20 milliseconds. A contact time less than 10 milliseconds is highly preferred. The duration or degree of contact is preferably regulated so as to produce a favorable balance between competing reactions and to produce sufficient heat to maintain the catalyst at the desired temperature.

[0064] In order to obtain the desired high space velocities, the process is operated at atmospheric or superatmospheric pressures. The pressures may be in the range of about

100 kPa to about 32,000 kPa (about 1-320 atm), preferably from about 200 kPa to about 10,000 kPa (about 2-100 atm).

[0065] The process is preferably operated at a temperature in the range of about 350°C to about 2,000°C. More preferably, the temperature is maintained in the range 400°C - 2,000°C, as measured at the reactor outlet.

[0066] The catalysts of the present invention should maintain hydrocarbon conversion of equal to or greater than about 85%, preferably equal to or greater than about 90% after 100 hours of operation when operating at pressures of greater than 2 atmospheres. Likewise, the catalysts of the present invention should maintain CO and H₂ selectivity of equal to or greater than about 85%, preferably equal to or greater than about 90% after 100 hours of operation when operating at pressures of greater than 2 atmospheres.

[0067] The synthesis gas product contains primarily hydrogen and carbon monoxide, however, many other minor components may be present including steam, nitrogen, carbon dioxide, ammonia, hydrogen cyanide, etc., as well as unreacted feedstock, such as methane and/or oxygen. The synthesis gas product, *i.e.*, syngas, is then ready to be used, treated, or directed to its intended purpose. The product gas mixture emerging from the syngas reactor may be routed directly into any of a variety of applications, preferably at pressure. For example, in the instant case some or all of the syngas can be used as a feedstock in subsequent synthesis processes, such as Fischer-Tropsch synthesis, alcohol (particularly methanol) synthesis, hydrogen production, hydroformylation, or any other use for syngas. One preferred such application for the CO and H₂ product stream is for producing, via the Fischer-Tropsch synthesis, higher molecular weight hydrocarbons, such as C₅₊ hydrocarbons.

[0068] Syngas is typically at a temperature of about 600-1500°C when leaving a syngas reactor. The syngas must be transitioned to be useable in a Fischer-Tropsch or other synthesis reactors, which operate at lower temperatures of about 200°C to 400°C. The syngas is typically cooled, dehydrated (*i.e.*, taken below 100°C to knock out water) and compressed during the transition phase. Thus, in the transition of syngas from the syngas reactor to for example a Fischer-Tropsch reactor, the syngas stream may experience a temperature window of 50°C to 1500°C.

Fischer-Tropsch Synthesis

[0069] The synthesis reactor using synthesis gas as feedstock is preferably a Fischer-Tropsch reactor. The Fischer-Tropsch reactor can comprise any of the Fischer-Tropsch technology and/or methods known in the art. The Fischer-Tropsch feedstock is hydrogen and carbon monoxide, *i.e.*, syngas. The hydrogen to carbon monoxide molar ratio is generally deliberately adjusted to a desired ratio of approximately 2:1, but can vary between 0.5 and 4. The syngas is then contacted with a Fischer-Tropsch catalyst. Fischer-Tropsch catalysts are well known in the art and generally comprise a catalytically active metal, a promoter and a support structure. The most common catalytic metals are Group VIII metals, such as cobalt, nickel, ruthenium, and iron or mixtures thereof. The support is generally alumina, titania, zirconia, silica, or mixtures thereof. In some embodiments, the catalyst is supported on a modified alumina as described in this invention. The preferred modifying agent is aluminum. Fischer-Tropsch reactors use fixed and fluid type conventional catalyst beds as well as slurry bubble columns. The literature is replete with particular embodiments of Fischer-Tropsch reactors and Fischer-Tropsch catalyst compositions. As the syngas feedstock contacts the catalyst, the hydrocarbon synthesis reaction takes place. The Fischer-Tropsch product contains a wide distribution of hydrocarbon products from C₅ to greater than C₁₀₀. The Fischer-Tropsch process is typically run in a continuous mode. In this mode, the gas hourly space velocity through the reaction zone typically may range from about 50 to about 10,000 hr⁻¹, preferably from about 300 hr⁻¹ to about 2,000 hr⁻¹. The gas hourly space velocity is defined as the volume of reactants per time per reaction zone volume. The volume of reactant gases is at standard pressure of 1 atm or 101 kPa and standard temperature of 0°C. The reaction zone volume is defined by the portion of the reaction vessel volume where reaction takes place and which is occupied by a gaseous phase comprising reactants, products and/or inerts; a liquid phase comprising liquid/wax products and/or other liquids; and a solid phase comprising catalyst. The reaction zone temperature is typically in the range from about 160°C to about 300°C. Preferably, the reaction zone is operated at conversion promoting conditions at temperatures from about 190°C to about 260°C. The reaction zone pressure is typically in the range of about 80 psia (552 kPa) to about 1000 psia (6895 kPa), more preferably from 80 psia (552 kPa) to about 600 psia

(4137 kPa), and still more preferably, from about 140 psia (965 kPa) to about 500 psia (3447 kPa).

[0070] For purposes of the present disclosure, certain terms are intended to have the following meanings.

[0071] “Active metal” refers to any metal that is present on a catalyst that is active for catalyzing a particular reaction. Active metals may also be referred to as catalytic metals.

[0072] A “promoter” is one or more substances, such as a metal or a metal oxide or metal ion that enhances an active metal’s catalytic activity in a particular process, such as a CPOX process or the Fischer-Tropsch process (*e.g.*, increase conversion of the reactant and/or selectivity for the desired product). In some instances a particular promoter may additionally provide another function, such as aiding in dispersion of active metal or aiding in stabilizing a support structure or aiding in reduction of the active metal.

[0073] A “modifying agent” is one or more substances, such as a metal or a metal oxide or metal ion that modify at least one physical property of the support material that it is deposited onto, such as for example structure of crystal lattice, mechanical strength, morphology.

[0074] With respect to the catalytic reaction such as partial oxidation of light hydrocarbons such as methane or natural gas to produce synthesis gas or conversion of synthesis gas to hydrocarbons, references to “catalyst stability” refer to maintenance of at least one of the following criteria: level of conversion of the reactants, productivity, selectivity for the desired products, physical and chemical stability of the catalyst, lifetime of the catalyst on stream, and resistance of the catalyst to deactivation.

[0075] A precursor or a compound of a metal is a chemical entity, such as, for example, a water-soluble metal salt, that contains the atoms of the metal (*e.g.*, a catalytic metal, a catalytic promoter, or a modifying agent) in an oxidation state that is not zero.

EXAMPLES

Preparation of modified alumina supports

[0076] The unmodified alumina support was obtained as γ -Al₂O₃ spheres with the following characteristics: a size in the range of 1.2 to 1.4 mm (average diameter of 1.3 mm.), a bulk density of 0.44 g/ml, a surface area and pore volume measure with N₂ adsorption of 143 m²/g and 0.75 ml/g respectively.

Example A: La₂O₃ modified Al₂O₃

[0077] The γ -Al₂O₃ spheres described above were impregnated with a aqueous solution containing desired amount of La(NO₃)₃ so that the La₂O₃ amount in the final material after drying and calcinations is approximately 3% by weight. The Al₂O₃ spheres impregnated with La(NO₃)₃ solution were dried in oven at 120°C overnight and then calcined at 1100°C for 3 hr. The La₂O₃-Al₂O₃ spheres (Catalyst Support, CS-1) were either subject to further modifications or used directly as catalyst support.

Example B: La₂O₃ modified Al₂O₃

[0078] The Al₂O₃ spheres described above were impregnated with a solution containing desired amounts of both La(NO₃)₃ and Al(NO₃)₃, and then the obtained material was dried overnight in an oven at 120°C for 3 hrs and calcined at 1100 °C for 3 hrs.

Example C: BaO modified Al₂O₃

[0079] The Al₂O₃ spheres described above were impregnated with a solution containing desired amount of Ba(NO₃)₂ and then the obtained material was dried at 120°C for 3 hrs and calcined at 1100 °C for 3 hrs.

[0080] Table 1 lists the BET surface areas, pore volume, average pore diameter, both measured by the BJH desorption method using N₂ as the adsorptive of commercially available unmodified γ -Al₂O₃ and modified Al₂O₃ catalyst supports. Surface area and pore size distribution are obtained on a Micromeritics TriStar 3000 analyzer after degassing the sample at 190°C in flowing nitrogen for five hours. Surface area is determined from ten points in the nitrogen adsorption isotherm between 0.05 and 0.3 relative pressure and calculating the surface area by the standard BET procedure. Pore size distribution is determined from a minimum of 30 points in the nitrogen desorption isotherm and calculated using the BJH model for cylindrical pores. The instrument control and calculations are performed using the TriStar software and are consistent with ASTM D3663-99 "Surface Area of Catalysts and Catalyst Carriers", ASTM D4222-98 "Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts by Static Volumetric Measurements", and ASTM D4641-94 "Calculation of Pore Size Distributions of Catalysts from Nitrogen Desorption Isotherms". The initial surface area of the catalyst is the surface area of the catalyst structure prior to contact of reactant gas. The pore volume of the catalyst (N₂ as adsorptive) is measured and calculated using the method

described above. Average pore size (diameter) based on N_2 adsorptive is calculated as $4V/A$.

TABLE 1: Surface area, pore volume and average pore diameter of support and catalyst examples after different calcination temperatures of the support.

Examples	Composition	Calcination Temp. of support, °C	BET SA, m^2/g	Pore volume, ml/g	Avg. pore diameter, nm
control	unmodified Al_2O_3	1100	80	0.54	21
		1200	16	0.19	45
A	La_2O_3 - Al_2O_3	1100	89	0.63	21
		1200	56	0.42	23
B	La_2O_3 - Al_2O_3 *	1100	87	0.57	20
C	BaO - Al_2O_3	1100	66	0.44	21
2	$Rh/Sm_2O_3/ La_2O_3$ - Al_2O_3	1100	71	0.54	24

* Prepared by impregnating Al_2O_3 with a solution containing $La(NO_3)_3$ and $Al(NO_3)_3$;

[0081] As shown in Table 1, modification of the Al_2O_3 with La_2O_3 (Examples A and B) increases the surface area of the material after calcinations at 1100°C (89 and 87 m^2/g vs. 80 m^2/g), while BaO modified Al_2O_3 (Example C) shows lower surface area than unmodified Al_2O_3 (66 m^2/g vs. 80 m^2/g). The two La_2O_3 modified Al_2O_3 samples prepared with different methods (with or without an aluminum oxide solution) show no significant difference in surface area (89 m^2/g vs. 87 m^2/g), but the Example A prepared with impregnating $La(NO_3)_3$ -only solution possesses greater pore volume than the Example B and its pore volume is also greater than that of unmodified Al_2O_3 as well (0.63 ml/g vs. 0.54 ml/g). Doping Al_2O_3 with BaO (Example C) reduces the total pore volume, which decreases from 0.54 ml/g to 0.44 ml/g.

[0082] As the data in Table 1 shows, the higher calcination temperature of 1200°C resulted in a significant reduction in BET surface area and pore volume, with a simultaneous increase of the average pore diameter for the unmodified alumina compared to the modified alumina. The BET surface area, pore volume, and average pore diameter for unmodified

alumina and Example A after calcination at 1200 °C are 16 and 56 m²/g , 0.19 and 0.42 ml/g, 45 and 23 nm respectively. Without the presence of the modifying agent, the phase transfer to α -alumina is more prevalent in unmodified alumina at this higher calcination temperature, and the high calcination temperature causes some micropores to collapse and therefore increase the pore sizes and decrease the surface area.

[0083] Modification of the Al₂O₃ with La₂O₃ does not change the pore diameter distribution significantly, as shown in Figure 1. The pore diameter is ~21 nm for the four catalyst supports listed in Table 2. The most probable average pore diameter is about 17 nm for unmodified Al₂O₃ and the two La₂O₃ modified Al₂O₃, while the most probable pore diameter of BaO modified La₂O₃ decreased to ~ 13 nm (Figure 1). The pore distribution curve of BaO modified Al₂O₃ (Example C) was shifted down to the direction of smaller sizes (Figure 1). Consequently, both the BET surface area and total pore volume of BaO-Al₂O₃ are lower than unmodified Al₂O₃.

[0084] The X-Ray Diffraction traces of unmodified Al₂O₃ and Examples A-C are shown in Figure 2. After calcinations at 1100°C, the commercially available Al₂O₃ consists of gamma, theta, alpha phases (γ , θ , and α respectively), with a significant presence of α phase. Compared with unmodified Al₂O₃, Examples A and B (La₂O₃ doped Al₂O₃) possesses less θ and almost no α phases, based on the relative intensity of XRD signals shown in Figure 2. As the phase transformations of Al₂O₃ follow $\gamma \rightarrow \theta \rightarrow \alpha$ with progressive heating, it can be concluded that modifying the Al₂O₃ with La₂O₃ inhibits the phase transformations from γ to θ to α , *i.e.*, modification of the Al₂O₃ stabilizes the structure of γ phase. Therefore, La₂O₃-Al₂O₃ (EXAMPLES A and B) maintains higher surface area than unmodified Al₂O₃ and it also preserves the original pore structure better after high temperature calcination (see Table 1 and Figure 1). On the other hand, doping the Al₂O₃ with BaO (EXAMPLE C) facilitate Al₂O₃ phase transformation to α phase. The signals of XRD peaks due to α phase Al₂O₃ are stronger and narrower in EXAMPLE C, (BaO modified Al₂O₃) as shown in Figure 2, reflecting the presence of significant α -Al₂O₃ phase in larger crystalline size compared to those present in unmodified Al₂O₃ and La₂O₃-Al₂O₃ materials (Example A and B). The predominant α -Al₂O₃ phase in BaO-Al₂O₃

explains that BaO-Al₂O₃ possesses a lower surface area than unmodified Al₂O₃ as BaO seems to de-stabilize the surface structure of γ -Al₂O₃ (Table 1).

Preparation of catalysts

EXAMPLE 1: 4%Rh/ La₂O₃-Al₂O₃

[0085] The La₂O₃-modified Al₂O₃ support material described as EXAMPLE A was impregnated with a RhCl₃ solution and the catalyst was dried in an oven overnight at 120°C, calcined in air at 900°C for 3 hrs and then reduced in H₂ at 600°C for 3 hrs. The Rh metal content in the catalyst was 4% by weight as calculated by mass balance. after drying and calcination

EXAMPLE 2: 4%Rh-4%Sm/ La₂O₃-Al₂O₃

[0086] The La₂O₃-modified Al₂O₃ support material obtained as EXAMPLE A was impregnated with a Sm(NO₃)₃ solution. The material was dried in oven for overnight at 120°C and then calcined at 1100°C for 3 hrs. The Sm content in the catalyst was 4 wt% Sm₂O₃ in the final material after drying and calcinations. The so-obtained Sm₂O₃/La₂O₃-Al₂O₃ catalyst precursor was impregnated with a RhCl₃ solution and the catalyst was dried in oven for overnight at 120°C, calcined at 900°C for 3 hr, and then reduced in H₂ at 600°C for 3 hrs to metallic Rh form before being charged into the reactor. The Rh metal content in the catalyst was 4% by weight again determined by mass balance.

EXAMPLE 3: 4%Rh-4%Sm/ La₂O₃-Al₂O₃

[0087] The catalyst sample was prepared similarly to Example 2, except the calcination temperature used for Sm₂O₃/La₂O₃-Al₂O₃ spheres was 1200°C (instead of 1100°C). The Rh metal content in the catalyst was 4% by weight in the final material after drying and calcinations.

EXAMPLE 4: 2%Rh-4%Sm/ La₂O₃-Al₂O₃

[0088] The catalyst sample was prepared similarly to Example 3 (calcination of Sm₂O₃/La₂O₃-Al₂O₃ spheres at 1200°C), except that the Rh metal content in the catalyst was 2% by weight in the final material after drying and calcinations.

EXAMPLE 5: 1%Rh-4%Sm/ La₂O₃-Al₂O₃

[0089] The catalyst sample was prepared similarly to Example 3 (calcination of Sm₂O₃/La₂O₃-Al₂O₃ spheres at 1200°C), except that the Rh metal content in the catalyst was 1% by weight in the final material after drying and calcinations.

EXAMPLE 6: 4%Rh-4%Ru/La₂O₃-Al₂O₃

[0090] A rhodium alloy catalyst was prepared with the method described in EXAMPLE 1. The La₂O₃ modified Al₂O₃ spheres (from EXAMPLE A) were impregnated with a solution containing both RhCl₃ and RuCl₃ such that to achieve 4 wt% for both Rh and Ru. The conditions for drying, calcination, reduction, are the same as those described in Example 1. The Rh and Ru content of the catalyst was 4 wt% for each metal in the final material after drying and calcinations.

EXAMPLE 7: 3.3%Rh/3.7%Sm on Co-modified Alumina

[0091] A catalyst containing 3.3% Rh/3.7% Sm on a 2.19% Co modified alumina support was prepared as follows. Tri-lobe gamma alumina (Sud Chemie, Inc. Louisville, KY) was crushed into 20-30 mesh size (0.595-0.841 mm range). An aqueous solution of a cobalt nitrate was applied to the gamma alumina material and dried using a rotary evaporator under vacuum and at a temperature of around 60°C. The drying was continued in an oven overnight at 90°C. The dried modified support was then heated up to 1100°C in air and held at 1100°C for four hours. Aqueous solutions of samarium nitrate and rhodium chloride were respectively applied to the support by impregnation, then the impregnated modified support was calcined by heating up to 700°C in air and held at 700°C for two hours after each impregnation. The Rh/Sm catalyst was then reduced at 500°C for three hours in a combined 300ml/min nitrogen and 300ml/min hydrogen stream. The resulting catalyst had the following composition of 3.3% Rh/3.7% Sm on a 2.19% Co modified alumina support of 30-50 mesh size (0.297-0.595 mm). Physical and morphological characteristics of the support and the resulting catalyst are given in Table 2. X-ray diffraction analysis of this sample revealed corundum alumina (alpha) and CoAl₂O₄/Co₃O₄ spinel in a very distinct pattern. CoAl₂O₄ spinel was the major component. Apparently due to the small crystalline size, both Sm and Rh were undetectable.

EXAMPLE 8: 3.3%h/1.9%Sm on Mg modified alumina

[0092] A catalyst containing 3.3% Rh/1.9% Sm on a 5.1% Mg modified alumina was prepared by similarly like EXAMPLE 7 except that the cobalt nitrate solution was replaced by a magnesium nitrate solution. The particle size of resulting catalyst was again 30-50 mesh (0.297-0.595 mm). Physical and morphological characteristics of the support and the resulting catalyst are given in Table 2. Upon X-ray diffraction analysis, this sample

revealed corundum alumina (alpha) and MgAl_2O_4 spinel components in a very distinct pattern. Again, the Sm and Rh components were not found due to the small crystalline size.

EXAMPLE 9: Rh/Sm on Si Modified Alumina

[0093] A catalyst comprising 3.7% Rh/3.7% Sm on Si modified alumina was prepared by similarly like EXAMPLE 7 except that the Co nitrate solution was replaced by a sodium silicate solution (from Aldrich). The particle size of resulting catalyst was again 30-50 mesh. Physical and morphological characteristics of the support and the resulting catalyst are given in Table 2. X-ray diffraction analysis indicates that the Si impregnated sample was still mainly in the gamma alumina form, the Si component being very difficult to identify. As in EXAMPLES 7 and 8, Sm and Rh were not apparent due to the small crystalline size.

[0094] Catalyst compositions, metal surface area, and metal dispersion for catalyst EXAMPLES 1-9 are summarized in the Table 2 below.

[0095] The metal surface area of the catalyst is determined by measuring the dissociative chemical adsorption of H_2 on the surface of the metal. A Micromeritics ASAP 2010 automatic analyzer system is used, employing H_2 as a probe molecule. The ASAP 2010 system uses a flowing gas technique for sample preparation to ensure complete reduction of reducible oxides on the surface of the sample. A gas such as hydrogen flows through the heated sample bed, reducing the oxides on the sample (such as platinum oxide) to the active metal (pure platinum). Since only the active metal phase responds to the chemisorbate (hydrogen in the present case), it is possible to measure the active surface area and metal dispersion independently of the substrate or inactive components. The analyzer uses the static volumetric technique to attain precise dosing of the chemisorbate and rigorously equilibrates the sample. The first analysis measures both strong and weak sorption data in combination. A repeat analysis measures only the weak (reversible) uptake of the probe molecule by the sample supports and the active metal. As many as 1000 data points can be collected with each point being fully equilibrated. Prior to the measurement of the metal surface area the sample is pre-treated. The first step is to pretreat the sample in He for 1 hr at 100°C . The sample is then heated to 350°C in He for 1 hr. These steps clean the surface prior to measurement. Next the sample is evacuated to sub-atmospheric

pressure to remove all previously adsorbed or chemisorbed species. The sample is then oxidized in a 10% oxygen/helium gas at 350°C for 30 minutes to remove any possible organics that are on the surface. The sample is then reduced at 400°C for 3 hours in pure hydrogen gas. This reduces any reducible metal oxide to the active metal phase. The sample is then evacuated using a vacuum pump at 400°C for 2 hours. The sample is then cooled to 35°C prior to the measurement. The sample is then ready for measurement of the metal surface. From the measurement of the volume of H₂ uptake during the measurement step, it is possible to determine the metal surface area per gram of catalyst structure by the following equation.

$$MSA = (V)(A)(S)(a)/22400/m$$

where MSA is the metal surface area in m²/gram of catalyst structure;

V is the volume of adsorbed gas at Standard Temperature and Pressure in ml.;

A is the Avogadro constant;

S is the stoichiometric factor (2 for H₂ chemisorption on rhodium);

m is the sample weight in grams; and

a is the metal cross sectional area.

[0096] As shown in Table 2, in which the metal in the equation is rhodium, the presence of samarium oxide (Sm₂O₃) helps to increase metal dispersion and metal surface area on the support Example A.

[0097] For the Rh-only catalysts with a rhodium metal dispersion measurement, *i.e.*, Example 1 (4%Rh/La₂O₃-Al₂O₃) and Example 2 (4%Rh-4%Sm/La₂O₃-Al₂O₃), the presence of Sm₂O₃ almost doubles the Rh metal dispersion from 4.5% to 8.5%. The Applicants believe that additional deposit of Sm₂O₃ on the La₂O₃-modified Al₂O₃ may further strengthen the interaction of rhodium with the support and thus help Rh dispersion.

TABLE 2: Catalyst Compositions for Examples 1-9 (on modified Al₂O₃), metal surface area, and rhodium dispersion.

CATALYST EXAMPLE S	Modifying agent	Active metal loading, wt%	Promoter Loading, wt%	Metal Surface Area, -m ² /g catalyst structure	Metal dispersion – rhodium, %
1	La	4 %Rh	0 % Sm	0.8	4.5
2	La	4 %Rh	4% Sm	1.5	8.5
3	La	4 %Rh	4% Sm	0.53	3.0
4	La	2 %Rh	4% Sm	0.35	5.5
5	La	1 %Rh	4% Sm	0.35	8.0
6	La	4 %Rh + 4% Ru	0% Sm	1.3	3.7
7	Co	3.33 %Rh	3.7 % Sm	3.3	-
8	Mg	3.3% Rh	1.9% Sm	7.7	-
9	Si	3.7% Rh	3.7% Sm	0.63	-

[0098] Referring back to Figure 1 which shows the pore size distribution of the catalyst Example 2, introducing Sm₂O₃ and/or Rh on La₂O₃-Al₂O₃ caused almost no change to the probabilities of pores with diameter greater than 20 nm, as one compares the pore distribution curves of support Examples A or B (La₂O₃-Al₂O₃) and catalyst Example 2 (4%Rh-4%Sm/ La₂O₃-Al₂O₃); however, the probabilities of pores with diameter less than 20 nm decreased significantly. It is likely that Rh and Sm₂O₃ coated preferentially on walls of <20 nm pores and reduced the pore diameter of those pores on support surface.

[0099] The BET surface area, pore volume and average pore diameter were determined for catalyst Example 2 (see Table 1) and can be compared to those of the support Example A that was used to make it. Both pore volume and BET surface area decrease compared to those of the support (89 versus 89 m²/g and 0.63 versus 0.54 ml/g respectively) whereas the average pore diameter increases (24 versus 21 nm), which is expected after deposition of both metals (Rh and Sm). The BET surface area is still quite high despite metal deposition and additional calcination steps at temperatures greater than 800°C.

[00100] A temperature-programmed reduction was also performed for catalyst Examples 1, 2 and 6. The TPR traces of 3 catalyst examples supported on La₂O₃-Al₂O₃, one with

rhodium (Example 1), one with rhodium and Sm_2O_3 (Example 2), and one with a rhodium-ruthenium alloy (Example 6). The reduction of Examples 1, 2 and 6 started at temperatures of 150, 157, and 153°C respectively. The reduction peak temperature was 177, 183, and 183°C, respectively, again for Example 1, 2 and 6.

[00101] For the alloy-containing Example 6, the reduction peak shape is quite symmetrical. The single symmetrical reduction peak in the TPR trace suggests that the Rh and Ru oxide species in this sample are in intimate contact or may even form a bulk compound in calcinations step; thus, H_2 may spillover from one site to sites of different nature once the reduction begins. As a result, only one single reduction peak was observed for the reduction of different oxide species (Rh and Ru).

[00102] For the Rh-only Examples 1 and 2, the presence of Sm species caused the reduction of Rh species to become more difficult – the reduction starts at higher temperature (150°C vs. 157°C) and the reduction peak position was also shifted from 177°C to 183°C for Example 2 with Sm_2O_3 addition. The difficulty of reduction for Example 2 compared to the reduction of Example 1, indicates that the interaction between Rh species and support surface is stronger in the Example 2 [4%Rh-4%Sm/ La_2O_3 - Al_2O_3] than that in Example 1 [4%Rh/ La_2O_3 - Al_2O_3]. Again, the stronger Rh metal and support interaction in Example 2 may contribute to its higher Rh dispersion on surface and metal surface area than that of Example 1 (see Table 2).

FIXED BED REACTIVITY TESTING

[00103] These catalyst Examples 1-9 were tested with molecular oxygen and natural gas as the hydrocarbon feed with a typical composition of about 93.1% methane, 3.7 % ethane, 1.34% propane, 0.25 % butane, 0.007% pentane, 0.01% C_{5+} , 0.31% carbon dioxide, 1.26% nitrogen (with % meaning volume percent). The hydrocarbon feed was pre-heated at 300°C and then mixed with O_2 . The reactants were fed into a fixed bed reactor at a carbon to O_2 molar ratio of 1.87 or a O_2 :natural gas mass ratio of 1.05 at gas weight hourly space velocities (GHSV) from about 161,000 to about 635,000 hr^{-1} . The gas hourly space velocity is defined by the volume of reactant feed per volume of catalyst per hour. The partial oxidation reaction was carried out in a conventional flow apparatus using a 12.7 mm I.D. quartz insert embedded inside a refractory-lined steel vessel. The quartz insert contained a

catalyst bed (comprising of 2.0 g of catalyst particles, except for Example 7 where 1.65 g was used) held between two inert 80-ppi alumina foams. The reaction took place for several days at a pressure of about 90 psig (722 kPa) for Examples 1-6 and for several hours at a pressure of about 4 psig for Examples 7-9, and at temperatures at the exit of reactor between about 750°C and about 1200°C. All the flows were controlled by mass flow controllers. The reactor effluent as well as feedstock was analyzed using a gas chromatograph equipped with a thermal conductivity detector. Pressures at the inlet and outlet on the reactor were measured by a differential pressure transmitter which gives the overall pressure drop across the catalytic bed by subtracting the pressure at the outlet from the pressure at the inlet.

[00104] The data analyzed include catalyst performance as determined by conversion and selectivity, and deactivation rate measured for some over a period of over 100 hours. The catalyst performances (CH₄ conversion, H₂ and CO selectivity) within a few hours after reaction ignition are listed in the following Table 3 for Examples 1-8 and the observed deactivation rates are listed in Table 4 for Examples 1, 2 and 6. Example 9 did not perform very well, and it should be noted that the metal surface area (ca. 0.63 m²/g catalyst structure) of this catalyst Example 9 may have been too low to be an effective catalyst in the partial oxidation of methane with oxygen.

Table 3: Test data with CH₄ conversion, CO and H₂ selectivity after 6 hours of reaction.

Catalyst Examples	GHSV, hr ⁻¹	CH ₄ conversion, %	CO selectivity, %	H ₂ selectivity, %
1	440,000	95	96	96
2	440,000	91	94	95
2*	440,000	94	97	97
3	675,000	91	96	95
4	635,000	91	95	94
5	635,000	93	94	96
6	438,000	91	96	95
7	161,000	95	96	89
8	175,000	96	97	90

*duplicate run

Table 4: Deactivation measured over a time period from 24 to 104 hours at a GHSV of about 440,000 hr⁻¹.

Catalyst Examples	Change in Pressure Drop, psi	CH ₄ conversion loss, %	CO selectivity loss, %	H ₂ Selectivity loss, %
1	0.68	3	1	1
2	0.02	2	1	0
2*	0.03	1	1	1
6	0.20	3	1	1

*duplicate run

[00105] As shown in Table 3, all Examples have very good overall catalytic performance towards syngas production. Examples 1 and 2 have the best methane conversion, whereas Examples 1, 2, 3, and 6 have very good selectivity for H₂ and CO. The oxygen conversion (not shown) was also measured for all tests, and was above 99% for all Examples. The best overall catalytic performance is best with Examples 1 and 2 among the catalysts studied (listed in Table 2). From Table 3, Example 2 runs clearly show the best reactor performance. For direct comparison run-to-run, the data were obtained at the same time on stream, for most runs from 6 to 104 hours after reaction initiation. The duplicate runs for Example 2 are nearly equivalent (see Table 3), demonstrating catalyst and reactor reproducibility.

[00106] Catalyst Examples 7 and 8 performance test results are also shown in Table 3. A catalyst containing 3.9% Rh/4.2% Sm on a Co modified alumina support was prepared the same way as Example 7 and performed similarly to Example 7 in the laboratory scale fixed reactor testing. A catalyst containing 3.7% Rh/3.8% Sm on a Mg modified alumina support was prepared the same way as Example 8 and performed similarly to Example 8 in the laboratory scale fixed reactor testing.

[00107] The change of the pressure drop over the course of the tests reported in Table 4 can be indicative of some catalyst deactivation. Increasing differential pressure may result from carbon deposition and/or poly-nuclear aromatic (PNA) formation on the catalyst surface or reactor system. Loss of methane conversion also can be indicative of formation of PNAs or PNA-precursors. As seen in Table 4, Example 2 appears to deactivate at a slower rate than Examples 1 and 6. Both runs for Example 2 show remarkable stability in pressure drop over time compared to the other catalyst examples 1 and 6. It is likely that Example 2 catalyst is less susceptible to carbonaceous deposit. Example 1 catalyst exhibits higher

loss of methane conversion than Example 2. Example 6 catalyst exhibits equivalent loss of methane conversion than Example 1.

[00108] Figure 3 shows the plots of the methane conversion and product selectivity for a typical test run of catalyst Example 2, demonstrating the great stability in partial oxidation of natural gas, with only 1% loss in methane conversion and product selectivity for the duration of the run (about 100 hours).

[00109] The examples and testing data show that the catalyst compositions of the present invention represent an improvement over prior art catalysts in their ability to resist deactivation over sustained time periods while maintaining high methane conversion and hydrogen and carbon monoxide selectivity values. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. The disclosures of all issued patents, patent applications and publications cited herein are incorporated by reference. The discussion of certain references in the Description of Related Art, above, is not an admission that they are prior art to the present invention, especially any references that may have a publication date after the priority date of this application.